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Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

ENERGY & ENVIRONMENT DIVISION

PARAMETRIC STUDY OF SUBMICRON PARTICULATES FROM PULVERIZED COAL COMBUSTION

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ABSTRACT

Pulverized coal sieved through a 200 mesh screen (particle diameter < 75 μ) was entrained in an air/methane/oxygen mixture and burned in an enclosed bunsen type burner fitted with a chimney. Measurements were made of the number and size of the particles in the submicron range (100 Å - 500 Å) downstream of the chimney exit using a transmission electron microscope. Variations in flame temperature (1900°K to 2500°K), cooling rate (3500 to 8000°K/sec) and oxygen concentration (equivalence ratio from .62 to .94) were made. Cold secondary air was injected at the chimney exit. Results showed a sharp peak in the particle size distribution at diameters below 200 Å for high cooling rates at high initial temperatures, suggesting homogeneous condensation of vaporized ash. At lower cooling rates the peak shifts toward larger particles. It appears possible, therefore, to control particulate emissions by modification of combustion and heat transfer conditions.

INTRODUCTION

During the combustion of pulverized coal the bulk of the mineral matter is converted to fly ash. A fraction of the mineral matter may be vaporized and subsequently condensed by homogeneous nucleation producing a large number of extremely small particles (1,2,3). The size of particles formed by homogeneous nucleation typically measure less than 1000 Å. Because of their small size these particles do not contribute substantially to the total mass of the ash and are often overlooked; however, they can be a significant fraction of the number of particles produced.

The submicron particles are most easily ingested into the lung and thus may be a greater health hazard than the larger particles. Also, certain toxic trace elements have been shown to be concentrated in the smaller ash particles (4,5) creating a health hazard greater than their prevalence might indicate. Electrostatic precipitators and other clean-up devices effectively remove large particles, but their efficiency decreases for small particles, allowing them to pass into the atmosphere (6). Because the mineral matter in the coal is necessarily converted to ash during combustion, it is preferable that the ash particles be large to reduce the health hazard and ease their removal from the stack gases.

This work consists of an experimental study of the effect of heat transfer and combustion parameters on the number and size distribution of particles in the submicron range, including consideration of practial methods of their control. The parameters that have been studied are the flame temperature, cooling rate and oxygen concentration

in the fuel lean range. Peak temperatures have been varied from 1900 K to 2500 K. By changing the thermal resistance of the burner chimney wall, cooling rates of 2500°K/sec. to 8000°K/sec. were obtained during the primary cooling period.

APPARATUS AND PROCEDURE

A small amount of Pittsburgh seam pulverized coal was entrained in an air/methane/oxygen mixture and burned in an enclosed bunsen type burner fitted with an insulated chimney. This arrangement was able to approximately simulate the temperature-time history of a pulverized coal boiler. The coal, whose properties are given in Table I, was already pulverized and was sieved through a 200 mesh screen to remove the larger particles. A simple vacuum sampler collected the smallest particles on a carbon film substrate for examination with a transmission electron miscroscope. Some preliminary work is reported in Ref. 7.

Equipment

A schematic diagram of the burner and sampler are shown in Fig. 1. Pulverized coal is entrained in a small amount of air in a hoper by using a jet of air to sweep coal particles from the surface of a fluidized bed. The coal hopper is placed on a balance to continuously determine the weight; all runs were standardized by burning one gram of coal.

The coal mixes with the methane, oxygen and additional air in a 10 mm diameter tube. A ceramic flameholder is inserted coaxially into the end of this tube and stabilizes the flame at the entrance to the ceramic chimney. The methane flame provides the hot, oxygen containing gas in which the coal particles burn. The chimney controls the rate at which the mixture cools; the residence time is sufficient for coal particle burn-out to occur in the first 1/4 to 1/3 of the chimney length. Three chimney configurations are used; an uninsulated ceramic tube 44 mm in diameter and 355 mm long, a similar tube provided with a layer of insulation to reduce heat loss and operate at higher temperatures, and a combined chimney that consisted of the insulated chimney plus an additional 180 mm section which is uninsulated. At the downstream end of each chimney, secondary air is injected so as to rapidly cool the products in a short, 75 mm length section (see Fig. 1). The sampling orifice is positioned 200 mm downstream of the chimney exit.

The sampler uses a small sonic orifice to aerodynamically separate the small particles. Near the orifice the flow accelerates rapidly; small particles are able to follow the flow and are drawn into the sampler. Because of their greater momentum, large particles cannot follow the accelerating flow and bypass the collector. Inside the collector (see Fig. 1) the particles are collected on a hexagonal cylinder; this collector geometry spreads the particles uniformly over the collection surface.

Procedure

Combustion and heat transfer conditions within the chimney are controlled by varying the methane/oxygen/air mixture and by varying the chimney configuration. A total flow rate of 30 ℓ/min through the burner is used in all runs, in addition, 30 ℓ/min of secondary air is injected at the end of the chimney. Approximately .2 sec are required for the products to travel to the point of secondary air injection. In the initial section of the chimney, cooling of the combustion gases is due to convection to the chimney wall. Increasing the concentration of methane from 8% to 12% increases the peak temperature from 1900°K to 2500°K; by keeping the coal flowrate small its effect on the temperature is minimized. The amount of oxygen used in each run is sufficient to: burn the methane in stoichiometric proportions; allow 1.0 ℓ/min to burn the .5 g/min flow of coal and provide 1.5 ℓ/min of excess oxygen. In the oxygen trials the quantity of excess oxygen is used as a parameter and is varied from .5 ℓ/min to 3.5 ℓ/min. The equivalence ratio is not a convenient parameter because it is difficult to relate it to conditions during the combustion of coal and it changes when the concentration of methane is varied. With constant excess oxygen supplied, the equivalence ratio changes from .79 to .85 as the methane concentration is changed from 8% to 12%. Table 2 lists the flowrates used for each run; the equivalence ratio and fraction of oxygen in the oxidizer are listed for reference. The equivalence ratio listed is based on two liters of oxygen per gram of coal, plus two liters of oxygen per liter of methane for stoichiometric conditions.

The temperature distributions in the chimney are shown in Fig. 2

for the different runs. Temperature measurements were made with a platinum/platinum - 10% rhodium thermocouple. Radiation from the thermocouple bead causes it to indicate a temperature below that of gas; a correction may be made by making a heat balance on the bead. For the thermocouple used in this investigation the correction is approximately 400°K and its uncertainty is estimated at $\pm$ 100°K.

In the initial section the cooling rate is moderate and approximately follows an exponential decrease along the chimney. For the insulated chimney, the temperature of combustion products decreases from 2500 to 1750°K in the runs using 12% methane, and from 1900 to 1400°K in the runs using 8% methane. Using the uninsulated chimney produced higher cooling rates and the temperature at the point of secondary air injection was approximately 1100°K for both the 8% and 12% methane runs. These decreases in temperature correspond to average cooling rates of 3000 to 5000°K/sec for the insulated chimney and 5000 to 8000°K/sec for the uninsulated chimney; the higher rate is for the run with 12% methane and lower for the run with 8% methane. The initial mixing of the secondary air with the hot products occurs over an 80 mm section of the chimney and occurs in approximately 0.04 sec. There is further mixing downstream of the chimney.

In summary, the temperature measurements indicate that the lowest cooling rate is obtained while using the insulated chimney, as expected, but the highest cooling rate also occurs with the insulated chimney during the injection of cold secondary air.

The temperature distribution in the combined chimney is initially the same as the distribution in the insulated chimney. The additional

section increases the residence time in a region of high temperature and moderate cooling rate. It also results in an exit temperature only slightly higher than is obtained with the uninsulated chimney.

The sampling procedure involves collecting a sample of ash while one gram of coal is burned. Examination of the sample requires a transmission electron microscope to study particle morphology in the 100 Å size range. To use the electron microscope the particles must be supported on a smooth film which is transparent to the electron beam. This film is produced by evaporating a thin (100 Å) carbon layer onto the surface of a mica sheet. The particles are nearly transparent to the electron beam; hence, a thin layer of opaque material is evaporated onto the sample to improve contrast. In this process, called shadowing (8), chromium is evaporated at an angle to the surface so that no material reaches the region behind the particle. The length of the white shadow indicates particle height and gives a three-dimensional effect. This can be seen in the micrographs (Figs. 5-8). Note that the gray background is the shadowing material.

MEASUREMENTS

The electron micrographs have been enlarged to a magnification of 200,000 for measurement purposes. In most cases a single micrograph, observed to be typical of many grid areas scanned, contains enough particles for counting. The actual particle counts are shown in Table 3. Also included in this table are the total particle counts,

and the total volume of the particles. The volume is a relative measure determined by multiplying by the diameter cubed. If the density is constant, it is also a measure of the mass of particulates. The data from selected runs is also presented in the form of histograms in Figs. 3a, b, c and 4a, b, c. The standard plot format for aerosols is to plot $\Delta N/\Delta \ln D$ vs. D on log-log paper. This format has been modified slightly to avoid difficulties with zero particle counts. The histograms in this report use $1 + \Delta N/\Delta \ln D$ rather than $\Delta N/\Delta \ln D$. With this format zero particle counts plot as 1.0 rather than negative infinity. The change in format also prevents the logarithmic scale from magnifying insignificant differences when the particle count is small. The curves drawn through the data in Fig. 3 were fitted by hand. However, in a majority of the cases a least squares fit using a cubic polynomial accurately reproduced the curves shown.

All of the runs that were found to be significant have been repeated. This data is included in Table 3 and is plotted in the form of histograms using the same format as the original data in Fig. 4.

RESULTS

A comparison of submicron size distribution for the three different cooling rate configurations, but at the same initial conditions (10% methane), is shown in Figs. 3a and 4a. The "insulated chimney" maintains a high temperature over the 355 mm length of ceramic chimney to the point where cold air is injected (at ~ 1600°K). The "uninsulated chimney" permits much faster cooling before the cold air injection (at

~ 1100°K). The "combined chimney" produces a longer residence time before cooling by injection of secondary air downstream. The comparison shows that removing insulation or providing a faster initial decrease in temperature produces a shift in the particle size distribution toward larger particles. The increase in residence time at high temperature appears to keep a peak in the size distribution toward the very small end but with fall-off at both the small and large ends making for a somewhat flatter distribution curve.

A comparison of size distributions for three peak temperatures (methane concentrations, Fig. 2) with relatively little initial cooling ("insulated chimney") is shown in Figs. 3b and 4b. The lowest flame temperature (8% methane) appears to produce a dramatic fall-off in the distribution above ~ 250 Å. As flame temperature increases the distribution widens with more larger particles, but with the peak retained at the very small particle size.

Figure 3c and 4c show the comparison for the three temperatures for faster initial cooling ("uninsulated chimney") with lower temperatures before the cold secondary air is injected. The peak of the size distribution shifts toward the larger sizes with increase in temperature.

Figures 5, 6, and 7 are the micrographs used to develop Fig. 3a; these figures show the decrease in the number of 100-200 Å particles between the insulated and uninsulated chimneys and the further reduction in the 200-500 Å particles when the combined chimney is used. Varying the amount of excess oxygen has only a small effect on the number and size distribution of the submicron particles and no trends were found.

In the course of this work micrographs were taken which provide direct evidence of the coalescence of ash particles. Many of the particles in Fig. 8 solidify before they become spherical and show that they were formed from smaller particles. The shadow of the large particle in the center shows that part of the particle is above the support film, held only by the rest of the particle. Figure 9 shows a scanning electron micrograph of a ~ 2 μ ash particle. The rough surface texture of this particle was formed when many submicron particles attached to its surface. This surface is not uncommon for spherical fly ash particles.

DISCUSSION OF RESULTS

The results of this experiment appear to be in agreement with a vaporization-condensation model for the formation of submicron ash particles (1,2,3). According to the model some of the volatile elements in the ash are vaporized in the high temperature region of the flame. Changes in the chemical state or a decrease in temperature cause the vapor to become supersaturated and condensation occurs. Submicron particles are formed by homogeneous nucleation and grow by condensation or by the coalescence of the particles. In competition with homogeneous nucleation, vaporized material may condense on the surface of existing ash particles; also submicron particles may coalesce with the large particles, reducing the quantity of submicron particles.

The effect of a low cooling rate inside the chimney, producing the largest number of particles in the size range between 100 and 200 Å,

suggests that these particles were formed in the downstream region of the burner. The high rate of cooling that occurs during the mixing of the combustion products with the cold secondary air causes ash remaining in the vapor phase to become highly super-saturated, resulting in homogeneous nucleation at this point. Because the temperature rapidly drops below the minimum temperature for particle coalescence, particles formed in this region remain in the small size range. A high temperature before secondary air injection increases the equilibrium concentration of vaporized ash and causes the rate of cooling due to the secondary air to be increased. These two effects, high temperature and fast mixing with cold air, combine to produce a high level of supersaturation which accounts for the observed peak in the particles collected downstream at 100-200 Å for high temperatures before secondary air injection. The insulated chimney produced the highest temperature prior to secondary air injection and hence a peak in the number of particles in 100-200 Å size range.

An increase in the peak temperature (higher methane concentration) also increases the temperature before secondary air injection but does not cause a simple increase in the number of 100-200 Å particles. An increase in peak temperature suggests increased vaporization or increased partial pressure of vaporized material. Increased partial pressure means a greater tendency for nucleation at a higher temperature. That may result in nucleation further upstream yielding larger particles downstream. If particles are formed upstream, they also provide sites for heterogeneous condensation with less likelihood of homogeneous nucleation downstream (9). An increase in flame temperature may also

mean more smaller particles as a result of higher vapor temperature when cold secondary air is injected. The final particle size distribution then depends on the effectiveness of the different competing processes.

Submicron particles larger than 200 Å appear to be formed upstream of the secondary air injection. This is suggested by the fact that the number and size distribution of the 250-500 Å particles were not affected by the cooling rate in the chimney. The particles may have formed in the primary flame zone where the conditions in both chimneys are similar, followed by growth of coalescence of the initial particles. In the primary flame zone the formation of the submicron particles may also be caused by nonuniform oxygen concentrations near the burning coal particles where oxygen may cause volatile compounds to become refractory. For example: SiO (volatile) + 1/2 O_2 → SiO_2 (refractory) (10). Micrographs (Fig. 7) showing coalesced particles also provide direct evidence that coalescence has occurred. If the chemical reactions described in Ref. 10 correctly describe the vaporization of silica, it would be necessary to modify the oxygen concentration in the immediate vicinity of a burning coal particle in order to affect the production of submicron particulates. The moderate changes in excess oxygen that have been investigated in this work would not be expected to produce changes in the atmosphere surrounding a burning coal particle and the results are consistent with this observation.

Increasing the residence time at high temperatures by using the combined chimney also substantially decreases the number of 250-500 Å particles relative to the results for the insulated chimney. If, as discussed above, the 250-500 Å particles are formed in the upstream

region of the chimney, the initial number of particles would be the same for the insulated and the combined chimneys. During the additional period of residence at high temperature many of these particles appear to have been removed from the flow. This is indicated in Fig. 3a for the run using 10% methane. The coalescence of the submicron particles with the larger fly-ash particles would reduce the number of particles observed. This process is also indicated by the observed surface texture of large fly ash particles, as shown in Fig. 9.

SUMMARY

The results of this experiment indicate that a fraction of the ash vaporized in a pulverized coal combustor condenses by homogeneous nucleation to form submicron particles. Many submicron particles may be formed in the primary flame zone. Additional submicron particles should be expected to be formed any time a rapid decrease in temperature occurs. The number of particles which appear to be formed near the primary flame zone is dependent on the flame temperature but is not affected by the cooling rate. A reduction in the peak temperature in a burner should reduce the production of submicron particles. For high initial temperatures a substantial fraction of the vaporized ash does not condense immediately but remains in the vapor phase until the products are cooled to a relatively low temperature. This vapor condenses by homogeneous nucleation to form submicron particles when extremely high cooling rates are encountered.

These results suggest that it may be possible to control submicron

particulate emissions by modifying combustion conditions. A low peak temperature would tend to reduce the amount of particulates. By avoiding rapid cooling in the heat exchanger the nucleation of additional particles should be avoided. If the residence time above the ash fusion temperature is increased, a reduction in submicron particulates through coalescence with larger ash particles may be possible.

ACKNOWLEDGMENT

This work was supported by the Division of Environmental Control Technology, Assistant Secretary for Environment, U.S. Department of Energy, under Contract #W-7405-ENG-48.

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TABLE 1

PITTSBURG SEAM COAL PROPERTIES

Proximate Analysis	moisture	1.6%
	volatile matter	35.8%
	fixed carbon	57.2%
	ash	5.4%
Ultimate Analysis	H	5.3%
	C	78.6%
	N	1.6%
	O	8.1%
	S	1.0%
	ash	5.4%

Estimated Size Distribution

Sieve Size		
On	Thru	% Weight
80	--	0.0
170	80	5.0
200	170	7.1
325	200	31.5
--	325	56.4

Table 2. Experimental Conditions: Fuel and Oxidizer Flow Rates

Methane Concentration %	Excess Oxygen ℓ/min	Flow Rates ℓ/min			Coal Flow Rate g/min	Equivalence Ratio*	$\frac{O_2}{O_2 + N_2}$
		Methane	Oxygen	Air			
8	0.5	2.4	0.6	27.0	0.5	0.92	0.23
8	1.5	2.4	1.9	25.7	0.5	0.79	0.26
8	3.5	2.4	4.4	23.2	0.5	0.62	0.34
9	1.5	2.7	2.7	24.6	0.5	0.81	0.24
10	1.5	3.0	3.6	23.4	0.5	0.82	0.32
11	1.5	3.3	4.4	22.3	0.5	0.84	0.34
12	0.5	3.6	4.0	22.4	0.5	0.94	0.33
12	1.5	3.6	5.3	21.2	0.5	0.85	0.37
12	3.5	3.6	7.8	18.6	0.5	0.70	0.44

$$\text{*Equivalence Ratio} = \frac{\frac{O_2}{\text{Fuel}}\ \text{Stoic.}}{\frac{O_2}{\text{Fuel}}\ \text{Supplied}}$$

Table 3. Particle Counts: number of particles per micrograph, of a given size

Experimental Conditions[a]	Median Diameter (Å)										Total Particle Count	Volume of Particles
	121	161	198	236	277	318	378	454	530	610		
12% CH_4, .5 ℓ/min oxygen	81	40	18	9	2	2	2	2			156	960
12% CH_4, 3.5 ℓ/min oxygen	123	51	4	4	2	1	1				187	680
11% CH_4	79	99	29	9	6	1	1				184	940
10% CH_4	119	75	33	15	3	1	1				247	1120
9% CH_4	79	56	47	25	4						209	1110
8% CH_4	49	31	18	1							100	410
8% CH_4, .5 ℓ/min oxygen	115	45	9	2							171	480
8% CH_4, 3.5 ℓ/min oxygen	85	41	21	4	3						154	600
12% CH_4, uninsulated chimney	2.0	2.5	2.5	1	4.5	1.5	3.0	1.5	1.5	0.5	20	850
10% CH_4, uninsulated chimney	6	7	2	11	2	3					31	350
8% CH_4, uninsulated chimney	19	14	9	1	1						44	200
10% CH_4, combined chimney	12	7	2	1	2						24	120
12% CH_4	77	51	21	17	13	8	3	3	1		194	1860
Repetition results												
12% CH_4	9	7	3	3	3	2	1	1	1	1	31	760
10% CH_4	6	7	8	3	2	1	1				29	270
8% CH_4	83	53	31	2							170	635
12% uninsulated chimney	2	2	4	2	1	1	3	2	1		18	620
10% uninsulated chimney	1	4	5	3	4	3	1				21	330
8% uninsulated chimney	5	2	2	1							10	50
10% combined chimney	8	6	2	3	1	1					21	150

[a] Insulated chimney 1.5 ℓ/min excess oxygen except as noted

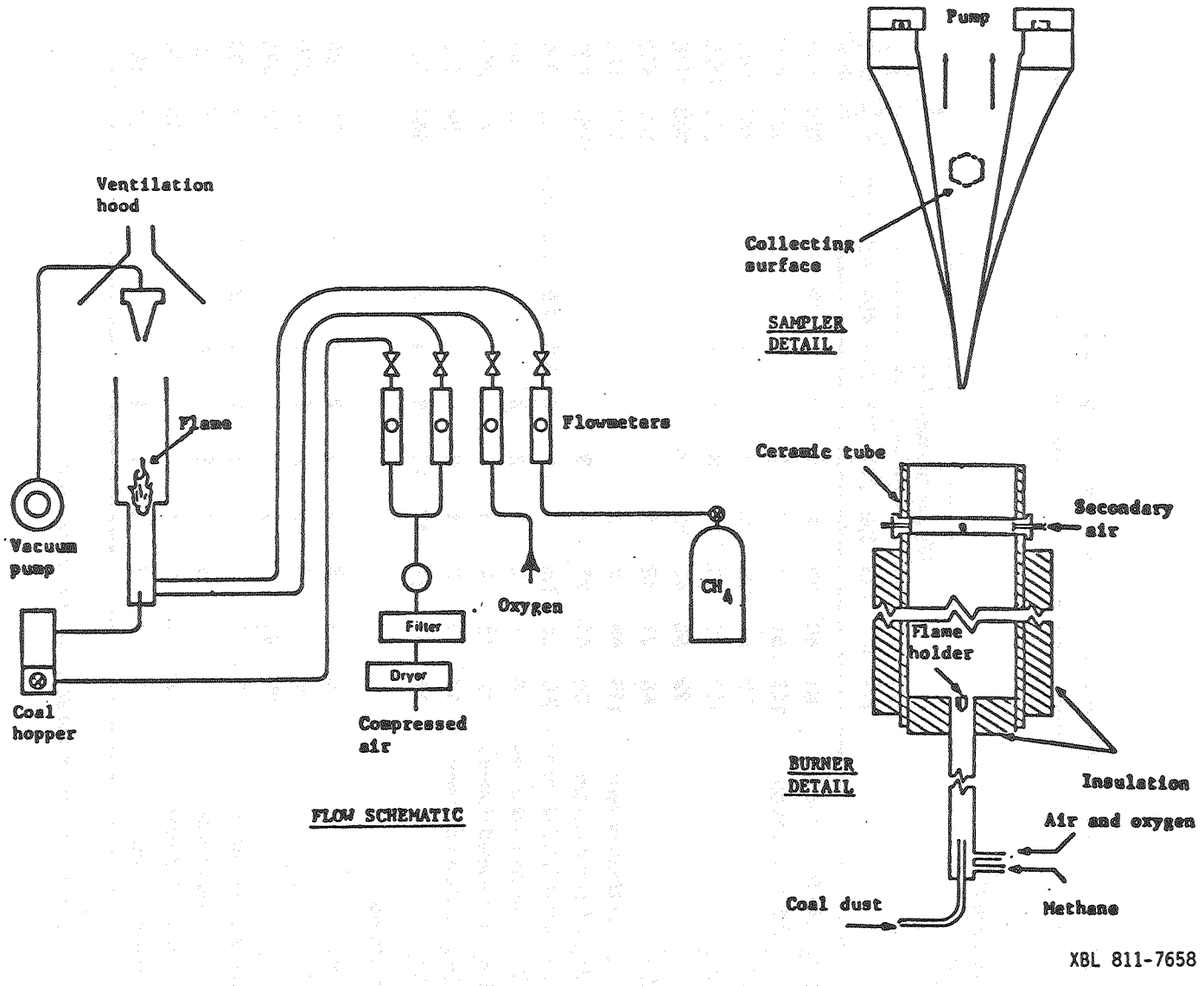


Figure 1 Experimental Apparatus

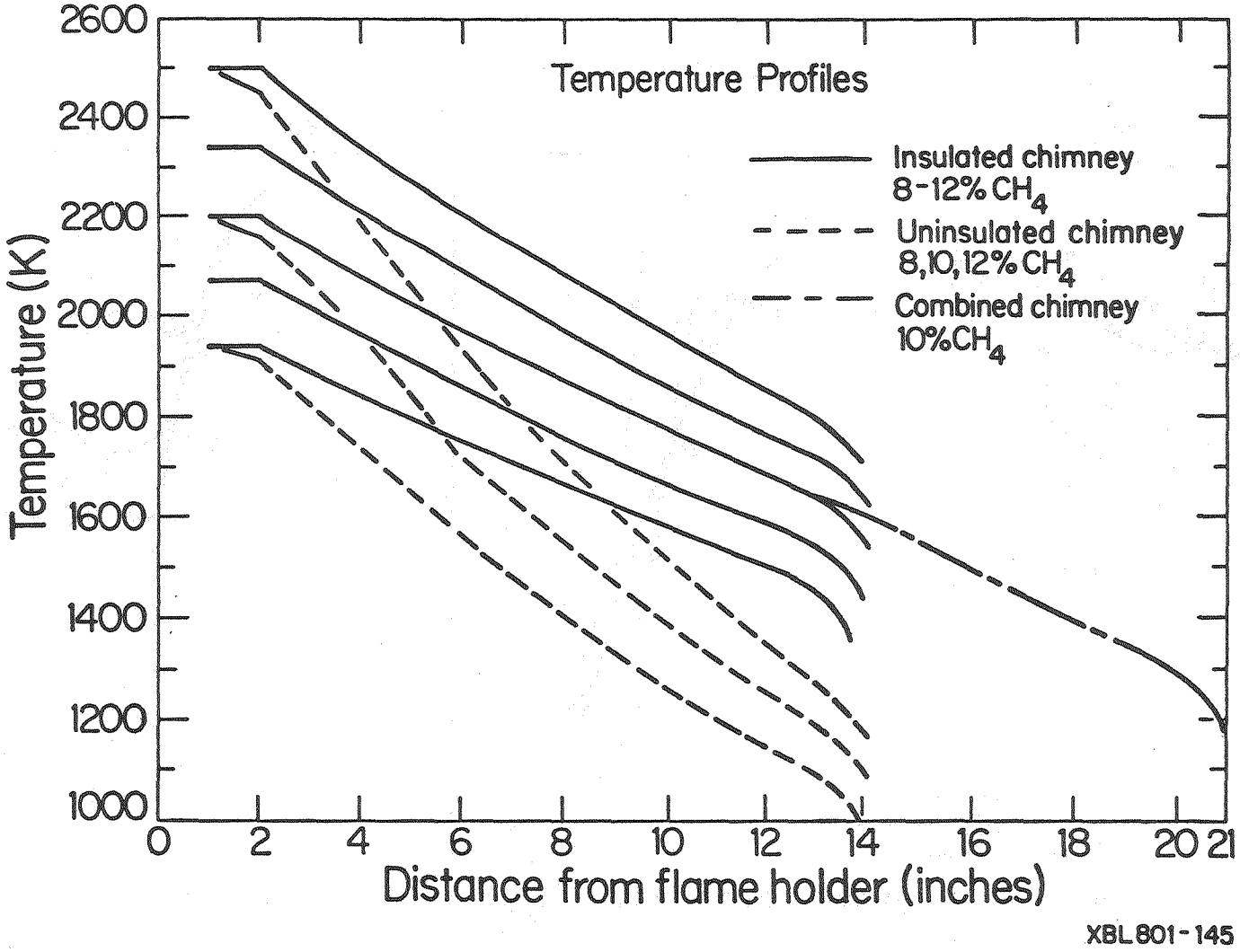


Figure 2 Chimney Temperature Profiles

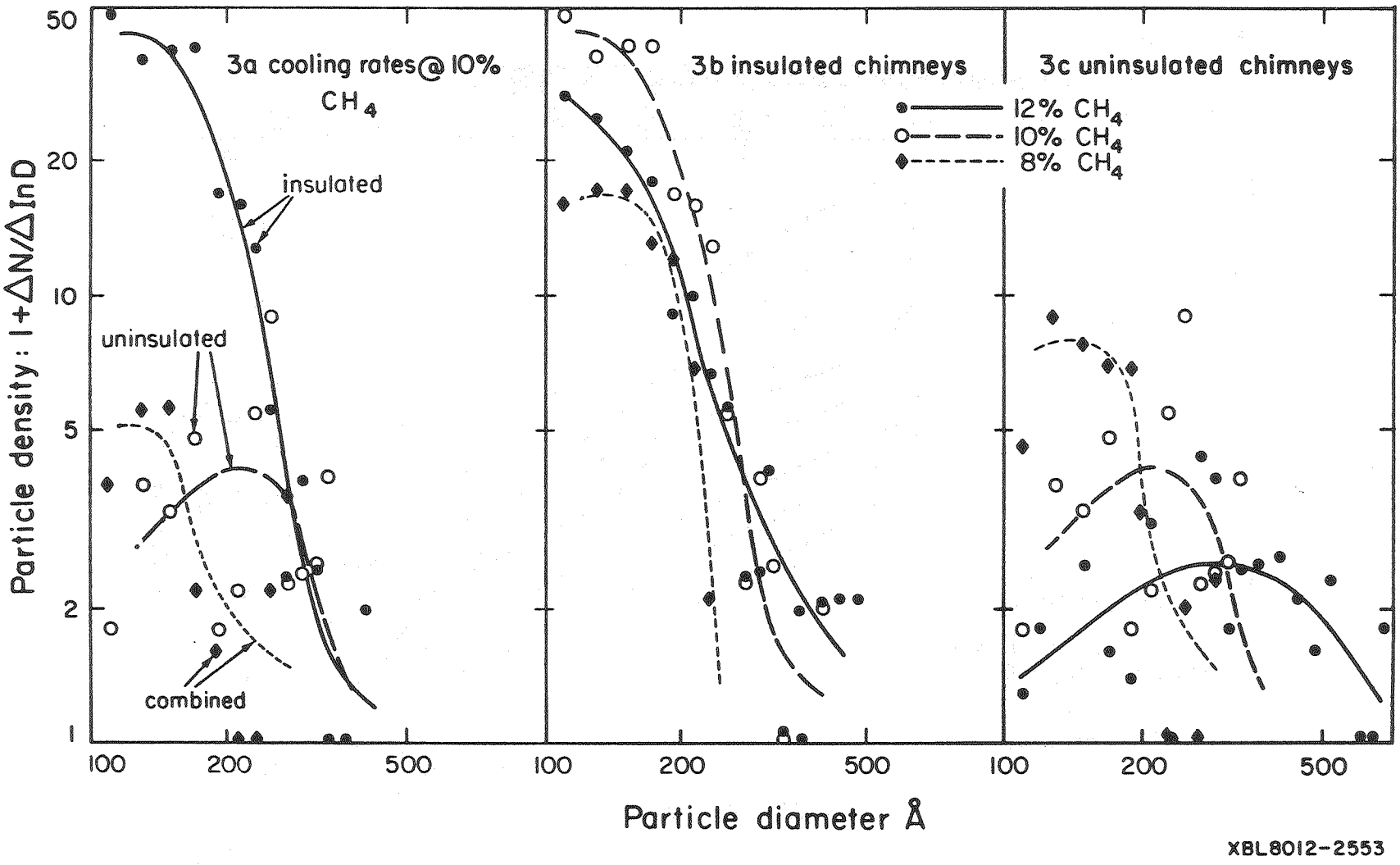


Figure 3. Particle Size Distribution

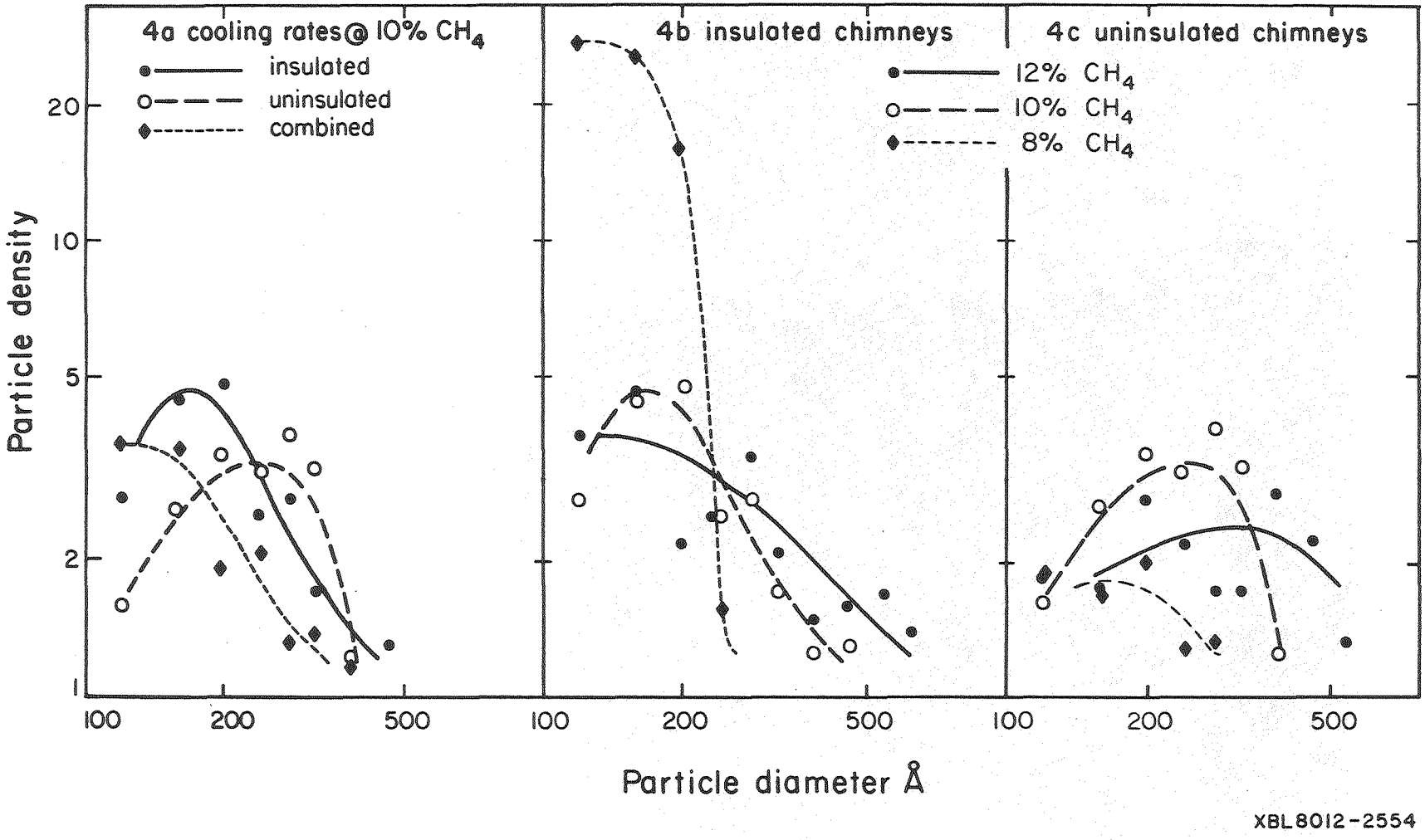
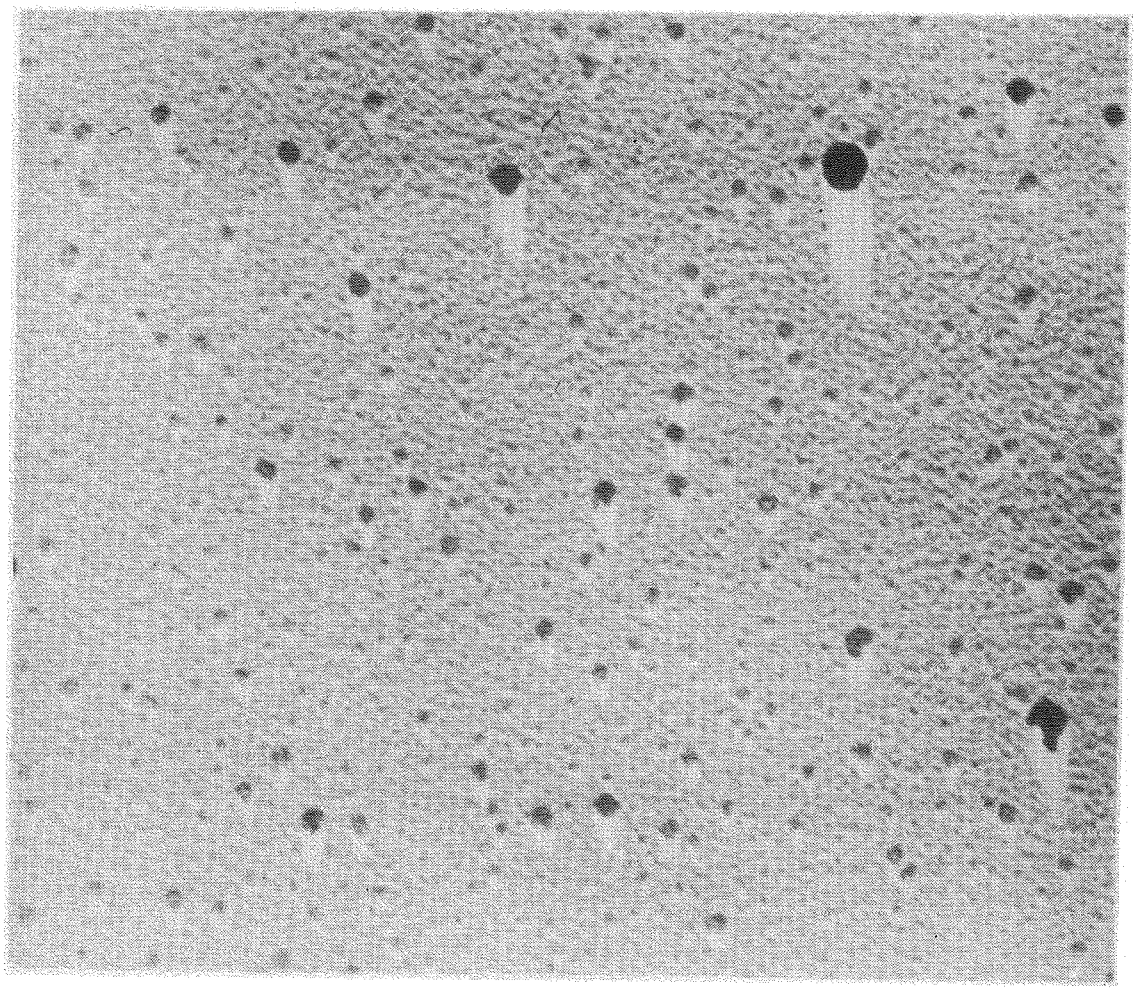


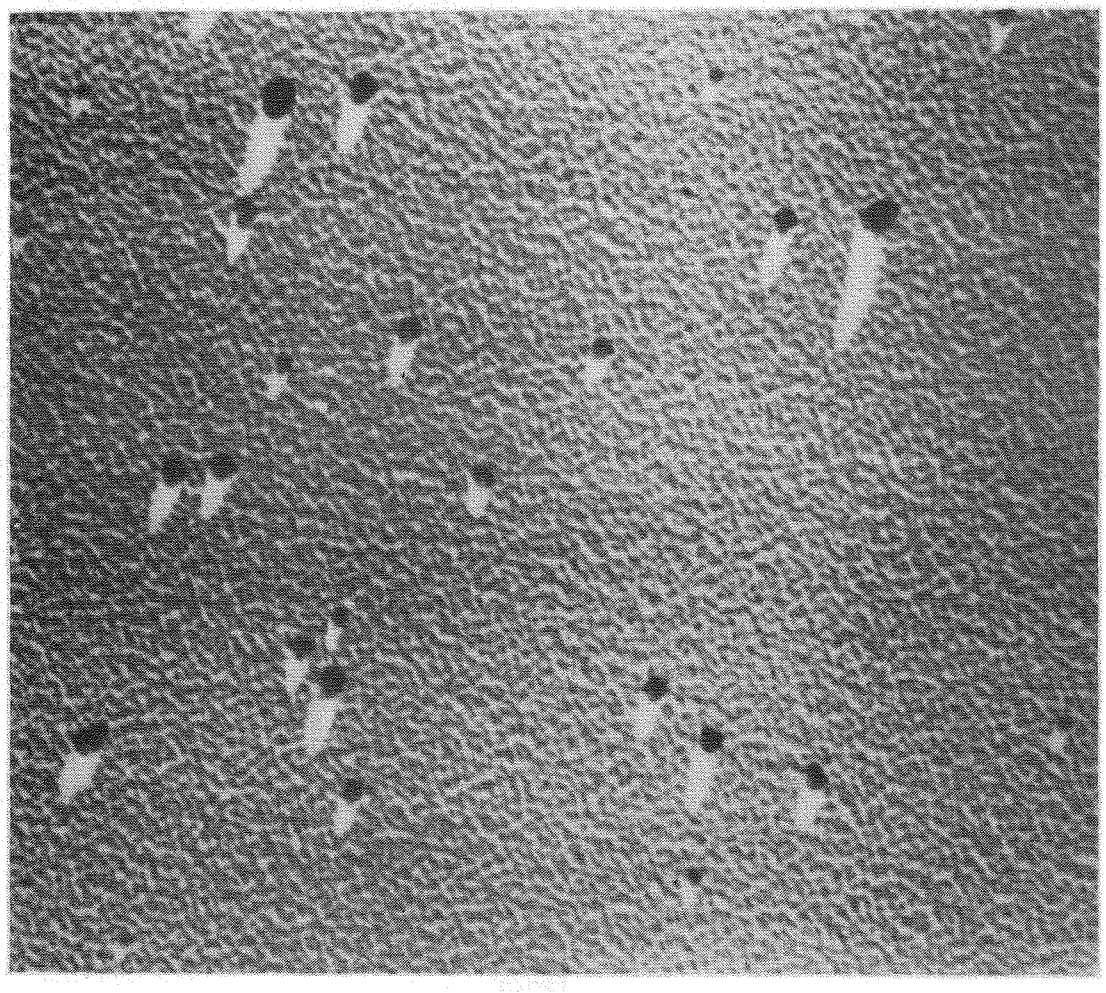
Figure 4. Particle Size Distribution



500 Å

XBB 801-657A

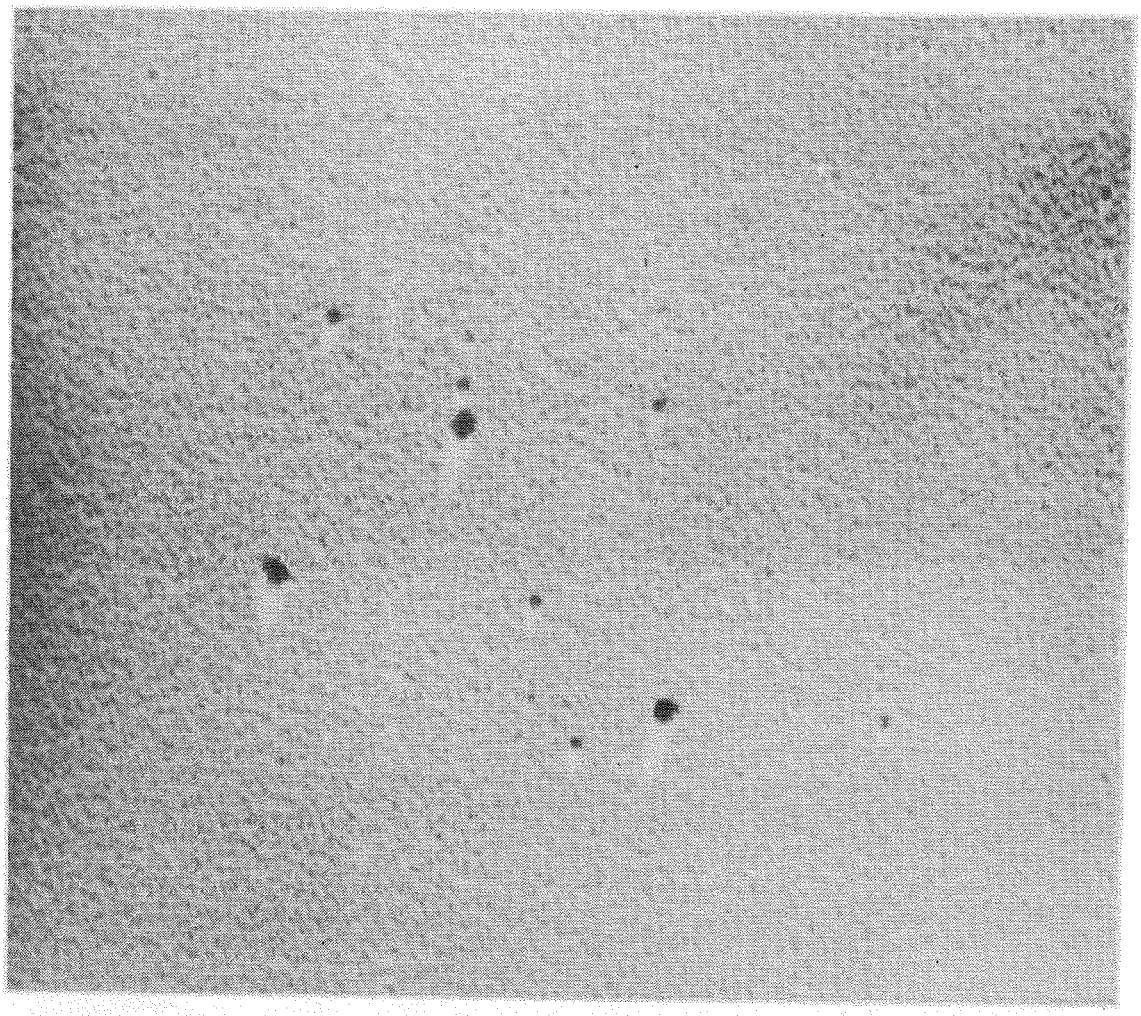
Figure 5 Micrograph of Particles (insulated chimnev, 10% Methane)



XBB 801-655A

500 Å

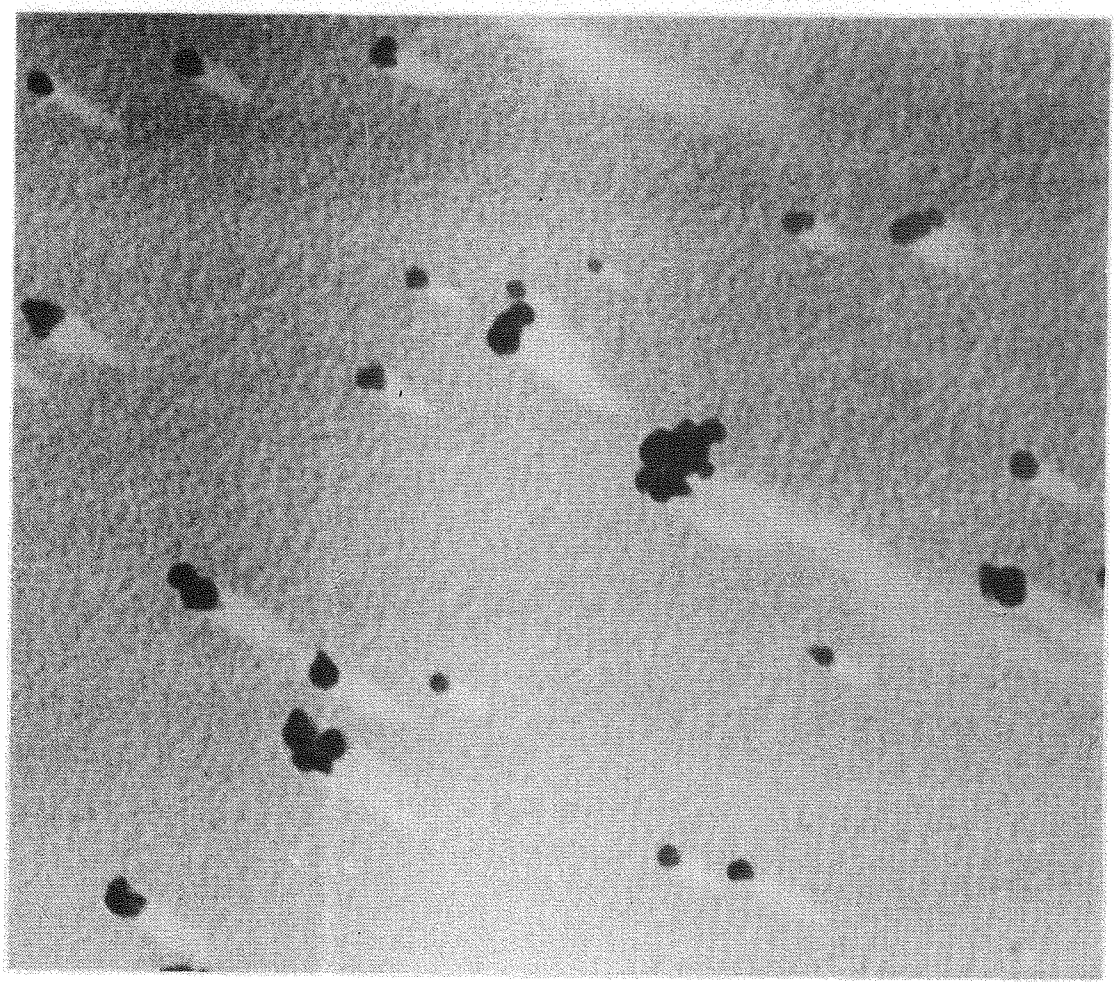
Figure 6 Micrograph of Particles (uninsulated chimney, 10% Methane)



500 Å

XBB 801-658A

Figure 7 Micrograph of Particles (combined chimney, 10% Methane)



500 Å

XBB 801-656A

Figure 8 Micrograph of Particles (uninsulated chimney, 12% Methane)

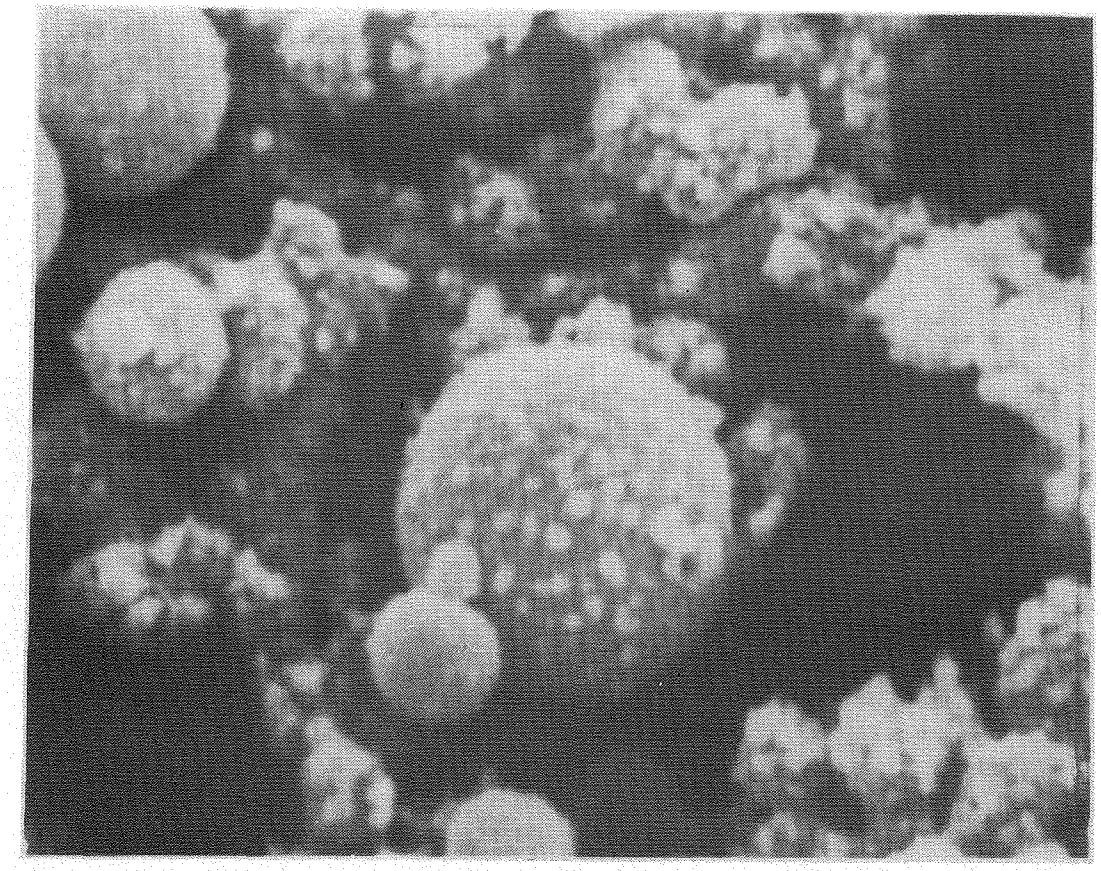


Figure 9 Scanning Electron Micrograph